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## Electrochemical Reduction of Chromate in the Presence of Nickel Chloride in Molten Lithium Chloride-Potassium Chloride Eutectic

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### ABSTRACT

Chronopotentiometry of chromate in the presence of  $\text{NiCl}_2$  in molten  $\text{LiCl-KCl}$  eutectic reveals a diffusion controlled, three electron reduction step. In the presence of excess  $\text{NiCl}_2$ , chromate is reduced at  $-0.35\text{V vs. Pt(II)/Pt}$  reference electrode and the electroactive species responsible for the chronopotentiometric wave is estimated to have a diffusion coefficient of  $1.06 \cdot 10^{-5} \text{ cm}^2 \text{ sec}^{-1}$  at  $450^\circ\text{C}$ . The stoichiometry of the reduction product depends mainly on the temperature at which the deposit is formed. At  $500^\circ\text{C}$  the deposit approaches the composition  $\text{LiNi}_2\text{CrO}_4$ . X-ray powder diffraction shows the deposit to be a single compound with a face centered cubic lattice. The length of the unit cell edge is estimated to be  $4.14\text{\AA}$ . At  $1400^\circ\text{C}$  a weight loss of the deposit is observed. X-ray powder diffraction shows the presence of two phases, which are identified as  $\text{NiO}$  and  $\text{NiCr}_2\text{O}_4$ . The weight loss is attributed to volatilization of  $\text{Li}_2\text{O}$ .

Laitinen and Propp (1) have shown that the electrochemical reduction product of  $\text{K}_2\text{CrO}_4$  in  $\text{LiCl-KCl}$  eutectic containing dissolved  $\text{MgCl}_2$  is a single unstoichiometric compound of formula  $\text{Li}_x\text{Mg}_y\text{CrO}_4$ , where  $x + 2y = 5$ . The values of  $x$  and  $y$  depended on the conditions of the electrolysis, namely current density, temperature, and the molar ratio of  $\text{Mg(II)}$  to  $\text{Cr(VI)}$  dissolved in the melt. Typical values of  $x$  ranged between 0.3 and 0.5.

Hanck (2) observed that the reduction of chromate in the presence of  $\text{Zn(II)}$  was shifted from  $-1.0\text{V vs. Pt(II)/Pt}$  reference to  $-0.5\text{V}$ . Analysis of the deposit indicated the composition to be  $\text{LiZn}_2\text{CrO}_4$ . The stoichiometry of the compound was not affected by the electrolysis conditions.

The present investigation was undertaken to determine whether the reduction of  $\text{K}_2\text{CrO}_4$  is affected by the presence of  $\text{NiCl}_2$  and to establish the composition of the reduction product. Spectrophotometric measurements failed to indicate any interaction between  $\text{Ni(II)}$  and chromate in the melt (3).  $\text{Ni(II)}$  is known to exist as stable chlorocomplexes (4) in chloride melts, and it was of interest to determine whether any chloride is contained in the deposit. Also the reduction potential of  $\text{Ni(II)}$  lies about  $0.2\text{V}$  below that of chromate in the absence of divalent ions and it was of interest to determine whether the deposition of metallic nickel could be avoided.

### Experimental

**Apparatus.**—A Hevi-Duty MK 3012-S vertical split tube furnace (Hevi-Duty Electric Company, Watertown, Wisconsin) was utilized in this work. The temperature sensing element was a chromel alumel thermocouple (Onega Engineering, Inc., Springdale, Connecticut). All experiments were made at  $450^\circ\text{C}$  except as noted.

A Sargent Model IV coulometric current source was used for the electrolytic preparation of the electrode deposits. The constant current source for the chrono-

potentiometric studies has been described previously (1).

A Tektronix 503 oscilloscope served to record chronopotentiograms and to monitor the potential of the working electrode continuously during the preparation of the electrode deposits. The Pyrex cell and envelope have been described previously (5).

**Electrodes.**—The Pt indicator electrode used in this study has been previously described (6). The electrode had a geometric area of  $0.5 \text{ cm}^2$  and was constructed so the glass metal seal was always kept above the level of the melt. The  $\text{Pt(II)/Pt}$  reference electrode was constructed as described by Ferguson (8).

The platinum gauze electrodes used to prepare samples of the film, as well as the carbon electrode which served as the counterelectrode in all electrochemical investigations in the melt, were constructed as described by Propp (1).

**Chemicals.**—All chemicals used in this study were reagent grade. Potassium chromate (J. T. Baker Chemical Company, Phillipsburg, New Jersey) was vacuum dried at  $150^\circ\text{C}$  before use. Anhydrous  $\text{NiCl}_2$  was prepared by heating the hexahydrate (J. T. Baker Chemical Company) in vacuum to  $180^\circ\text{C}$  over a three day period. Analysis indicated it to be 99.3% pure.

The  $\text{LiCl-KCl}$  eutectic was obtained from Anderson Physics Laboratories, Inc., Champaign, Illinois. The method of purification has been described (7).

Solid chemicals were added to the melt by means of a small glass spoon. A blanket of argon was kept over the melt at all times to exclude oxygen and water vapor. The purification train used in purifying the argon has been described (8).

**Experimental techniques.**—Samples of the electrode deposit resulting from the reduction of chromate in the presence of  $\text{NiCl}_2$  were obtained by constant current electrolysis using platinum gauze electrodes. The gauze electrodes were cleaned in boiling  $\text{HClO}_4$ , rinsed with distilled water, dried at  $120^\circ\text{C}$  for 16 hr, and weighed before their insertion into the molten salt solution. After electrolysis the gauze electrodes were

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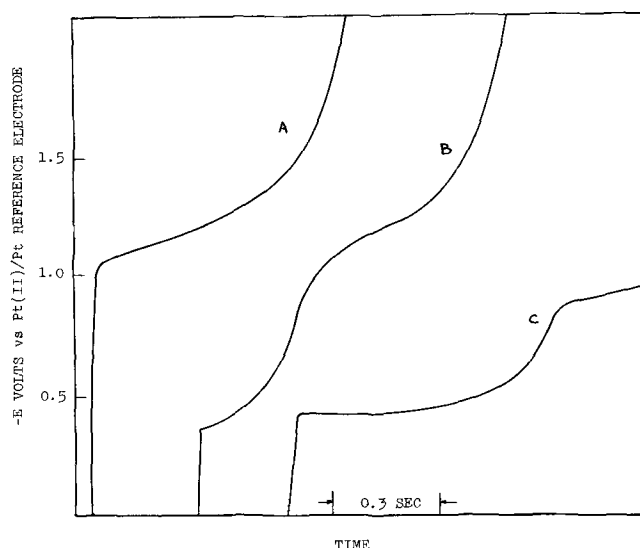


Fig. 1. Effect of nickel chloride concentration on reduction of chromate.  $1.56 \times 10^{-2} M$   $K_2CrO_4$ . A. No  $NiCl_2$ ; B.  $7.29 \times 10^{-3} M$   $NiCl_2$ ; C.  $3.28 \times 10^{-2} M$   $NiCl_2$ .

washed with deionized water, dried at  $120^\circ C$ , and reweighed. The electrode deposits were dissolved in boiling 72% perchloric acid. The nickel content of the deposit was determined by an EDTA titration using a murexide indicator. The method chosen for the chromium determination is a modification of that of Meier, Myers, and Swift (9). The procedure used has been previously described (1). Lithium was quantitatively determined by flame photometry.

### Results and Discussion

**Chronopotentiometry of  $K_2CrO_4$ - $NiCl_2$ - $LiCl$ - $KCl$  systems.**—The effect of  $Ni(II)$  on the reduction of chromate was demonstrated by successively increasing the concentration of  $Ni(II)$  at constant chromate concentration. Figure 1 shows that at a  $Ni(II)$  concentration of  $7.29 \times 10^{-3} M$ , two transitions were obtained: one at 0.35V vs.  $Pt(II)/Pt$  reference and the other at  $-1.0V$ . Additional increases in the nickel concentration caused the wave at  $-0.35V$  to grow larger. At a sufficiently high  $Ni(II)/Cr(VI)$  concentration ratio (2.1), the wave at  $-1.0V$  disappeared but a new wave appeared at approximately  $-0.85V$  which corresponds to the reduction of  $Ni(II)$ . Further increase in the  $Ni(II)$  concentration had no influence on the first reduction step. This can be seen from the fact that identical transition times were obtained for  $1.56 \times 10^{-2} M$   $K_2CrO_4$  solution containing  $3.28 \times 10^{-2} M$   $NiCl_2$  and for one containing  $5.6 \times 10^{-2} M$   $NiCl_2$ .

According to the Sand equation the product of  $i\tau^{1/2}$  is independent of  $i$  for a semi-infinite linear diffusion controlled process. The dependence of  $i\tau^{1/2}$  on  $i$  is demonstrated in Table I for the reduction of  $K_2CrO_4$

Table I. Chronopotentiometry of  $K_2CrO_4$  in the presence of  $NiCl_2$

$E_{T/4} = -0.35V$		Area of the Pt flag = $0.5 cm^2$			
$C_{K_2CrO_4}$ (M)	$C_{NiCl_2}$ (M)	$i$ (mA)	$\tau^{1/2}$ (sec <sup>1/2</sup> )	$i\tau^{1/2}$ (A sec <sup>1/2</sup> )	$i\tau^{1/2}/C$ (A sec <sup>1/2</sup> /cm <sup>3</sup> mole <sup>-1</sup> )
$7.8 \times 10^{-3}$	$1.34 \times 10^{-2}$	6.625	0.497	$3.29 \times 10^{-3}$	422
		5.0	0.665	$3.25 \times 10^{-3}$	426
		4.0	0.850	$3.40 \times 10^{-3}$	439
		3.33	1.00	$3.33 \times 10^{-3}$	427
		2.0	1.605	$3.20 \times 10^{-3}$	410
$1.56 \times 10^{-2}$	$5.67 \times 10^{-2}$	8.33	0.80	$6.664 \times 10^{-3}$	426
		10.0	0.656	$6.56 \times 10^{-3}$	427
		12.5	0.53	$6.63 \times 10^{-3}$	424
$2.30 \times 10^{-2}$	$5.67 \times 10^{-2}$	12.5	0.775	$9.68 \times 10^{-3}$	421
		16.7	0.565	$9.50 \times 10^{-3}$	412
		18.94	0.490	$9.77 \times 10^{-3}$	425
$2.75 \times 10^{-2}$	$5.67 \times 10^{-2}$	14.3	0.79	$11.3 \times 10^{-3}$	411
		16.7	0.67	$11.25 \times 10^{-3}$	410
		18.94	0.566	$11.30 \times 10^{-3}$	411

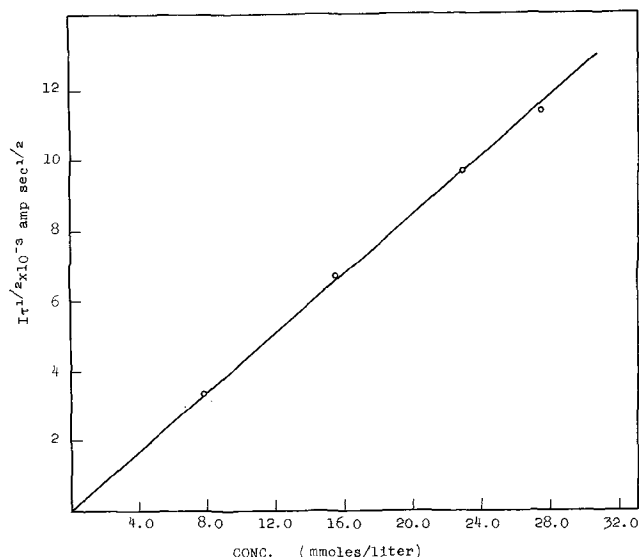


Fig. 2. Dependence of  $i\tau^{1/2}$  on concentration of  $K_2CrO_4$ .  $0.5 cm^2$  Pt flag electrode.  $C_{NiCl_2}/C_{K_2CrO_4} > 2.1$ .

in the range of  $7.8 \times 10^{-3} M$  to  $2.75 \times 10^{-2} M$ . The results indicate that the reduction of chromate in the presence of  $Ni(II)$  is diffusion controlled over the time interval investigated. Using  $n = 3$  from the controlled current coulometry, a value of  $4.19 \pm 0.010 \cdot 10^2 A sec^{1/2} cm^3 mol^{-1}$  for the transition time constant and  $0.5 cm^2$  for the area of the electrode, we calculate  $D = 1.06 \pm 0.06 \cdot 10^{-5} cm^2 sec^{-1}$  for the chromate reduction in the presence of  $Ni(II)$  at  $450^\circ C$ . From the slope in Fig. 2 (plot of  $i\tau^{1/2}$  vs.  $C$ ) the same value for the diffusion coefficient was obtained.

In order to establish the chemical composition of the electrode deposit, samples of the deposit, which had been prepared by constant current electrolysis over a wide range of preparative conditions were analyzed. To guard against the deposition of metallic nickel, the potential of the working electrode never was allowed to become more cathodic than  $-0.35$  vs.  $Pt(II)/Pt$ . The influence of temperature, current density, and molar ratio of  $Ni(II)$  to  $Cr(VI)$  on the deposit composition was studied.

While holding the current density and the  $Ni(II)$  to  $Cr(VI)$  ratio constant, a series of deposits was prepared at  $400^\circ$ ,  $450^\circ$ , and  $500^\circ C$ . The results of chemical analyses of these deposits are shown in Table II. From this table one can see that  $Li(I)$  content increases and the  $Ni(II)$  content correspondingly decreases as the temperature of the molten salt bath is increased. Table II also shows that the sum of the weight percentages of the three oxides,  $NiO$ ,  $Li_2O$ , and  $Cr_2O_3$  is very close to 100%, indicating that the chromium in the deposit is in the  $+3$  oxidation state, and that no chloride or potassium ion is present. The absence of chloride in the deposit requires that the nickel chloro-complex dissociate before the  $Ni(II)$  is incorporated into the deposit. That such a dissociation occurs rapidly enough to prevent inclusion of chloride in the deposit is remarkable. From Table II it is also obvious that in spite of the fact that the reduction potential of  $Ni(II)$  lies about 0.2V below that of chromate in the absence of divalent metal ions, no evi-

Table II. Composition of electrode deposit as function of temperature

$C_{K_2CrO_4} = 0.052M$		$C_{NiCl_2} = 0.198M$			
Temper- ature ( $^\circ C$ )	Wt % $Li_2O$	Wt % $NiO$	Wt % $Cr_2O_3$	Total %	Formula
400	3.75	66.8	31.90	102.0	$Li_{0.00}Ni_{2.10}CrO_{3.91}$
450	4.09	64.5	30.60	99.2	$Li_{0.02}Ni_{1.12}CrO_{3.86}$
500	5.10	64.0	31.90	101.0	$Li_{0.03}Ni_{1.08}CrO_{3.86}$

dence to the deposition of metallic nickel was obtained. The empirical formula which best describes the deposit composition is  $\text{Li}_{1.2}\text{Ni}_2\text{CrO}_4$ . As was observed by Propp (1) in his study of the  $\text{MgCl}_2$ - $\text{K}_2\text{CrO}_4$  system,  $x + 2y = 5$  indicating that no oxide is lost during the electrolysis. At high temperature the deposit approaches the composition  $\text{LiNi}_2\text{CrO}_4$ .

Table III indicates that there is only a small change in the composition of the electrode deposit on changing the molar ratio of Ni(II) to Cr(VI). There is a slight decrease in Li(I) content and an accompanying increase in Ni(II) content as the molar ratio of Ni(II) to Cr(VI) is increased. The effect of current density on the composition of the electrode deposit on holding the temperature and the molar ratio of Ni(II) to Cr(VI) constant was observed and is indicated in Table IV. Current density in the range 1-10 mA/cm<sup>2</sup> does not appear to be a significant factor in determining the chemical composition of the electrode deposit.

**X-ray powder diffraction studies.**—Table V indicates that the deposit is a single compound with a face centered cubic lattice. The length of the unit cell edge is estimated to be 4.14Å.

**Thermal stability of electrode deposit.**—A sample of deposit, while still on the platinum gauze electrode, was heated in air and in an argon atmosphere to 1000°C for a period of 48 hr. Weight losses were only 0.5% in argon and 0.04% in air. Chemical analyses on the heated samples were in agreement with the previous analyses of unheated samples. The heated samples contained 3.87%  $\text{Li}_2\text{O}$ , 66.7%  $\text{NiO}$ , and 37.50%  $\text{Cr}_2\text{O}_3$  corresponding to the empirical formula  $\text{Li}_{0.60}\text{Ni}_{2.11}\text{CrO}_{3.91}$ . The x-ray powder pattern of the deposit appeared to change slightly after heating to temperatures above 950°C. The original face centered cubic lines appeared to shift to give larger "d" spacings and diffuse lines were observed at 4.788 and 2.494Å.

A powdered sample of the deposit was heated to 1430°C in an air atmosphere. The x-ray diffraction pattern of the heated sample is shown in Table VI.

The pattern shows the presence of two phases; a diamond cubic phase with a unit cell edge of 8.305Å and a face centered cubic phase with a unit cell edge

Table V. X-ray data for electrode deposit

d (Å)	I/I <sub>0</sub>	hkl	a (Å)
2.3840	60	111	4.129
2.0657	100	200	4.137
1.4622	60	220	4.136
1.2476	30	311	4.178
1.1957	20	222	4.1403
1.0352	10	400	4.141

Table VI. X-ray powder pattern of electrode deposit heated to 1430°C

d (Å)	I/I <sub>0</sub>
4.7533	10
2.9180	15
2.493	100
*2.4024	60
*2.0798	40
2.0650	20
1.6960	30
1.5938	80
*1.4730	20
1.4696	100
1.2635	10
*1.2599	25
1.207	10
1.0798	10

\* Face centered cubic lines.

of 4.169Å. The face centered cubic phase corresponds reasonably well to  $\text{NiO}$  ( $a = 4.176\text{Å}$ ) and the diamond cubic phase to  $\text{NiCr}_2\text{O}_4$  ( $a = 8.32\text{Å}$ ). No lines were observed which could be assigned to the unheated nickel compound or to pure  $\text{Li}_2\text{O}$ .

Chemical analyses of the electrode deposit heated to 1400°C are in agreement with x-ray data. The deposit contained 67.01%  $\text{NiO}$ , 32.3%  $\text{Cr}_2\text{O}_3$ , and no  $\text{Li}_2\text{O}$ , which corresponds to the empirical formula  $\text{Ni}_{2.11}\text{CrO}_{3.61}$ .

The empirical formula of an unheated sample was found to be  $\text{Li}_{0.7}\text{Ni}_{2.10}\text{CrO}_4$ . If the  $\text{Li}_2\text{O}$  is lost during heating, the remainder of the compound must have the empirical formula  $\text{Ni}_{2.10}\text{CrO}_{3.6}$  which is in agreement with chemical analyses of the heated sample.

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Any discussion of this paper will appear in a Discussion Section to be published in the December 1970 JOURNAL.

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Table III. Composition of electrode deposit as function of  $\text{NiCl}_2$  concentration

Temperature = 450°C			I = 1.26 mA/cm <sup>2</sup>
$\text{C}_{\text{K}_2\text{CrO}_4}$ , M	$\text{C}_{\text{NiCl}_2}$ , M	Total Wt %	Formula
0.078	0.152	100.1	$\text{Li}_{0.71}\text{Ni}_{2.06}\text{CrO}_{3.94}$
0.068	0.225	99.8	$\text{Li}_{0.65}\text{Ni}_{2.10}\text{CrO}_{3.94}$
0.058	0.312	99.1	$\text{Li}_{0.62}\text{Ni}_{2.12}\text{CrO}_{3.94}$
0.056	0.481	99.0	$\text{Li}_{0.62}\text{Ni}_{2.15}\text{CrO}_{3.98}$

Table IV. Effect of current density on composition of electrode deposit

$\text{C}_{\text{K}_2\text{CrO}_4} = 0.0482\text{ M}$	$\text{C}_{\text{NiCl}_2} = 0.124\text{ M}$	Temperature = 450°C	
I, mA/cm <sup>2</sup>	Total Wt %	Formula	
1.21	99.2	$\text{Li}_{0.66}\text{Ni}_{2.15}\text{CrO}_{3.95}$	
2.82	99.2	$\text{Li}_{0.63}\text{Ni}_{2.19}\text{CrO}_{4.00}$	
4.31	98.5	$\text{Li}_{0.58}\text{Ni}_{2.20}\text{CrO}_{3.99}$	
9.82	98.9	$\text{Li}_{0.58}\text{Ni}_{2.19}\text{CrO}_{3.98}$	